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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US95/02799 <b>(22) International Filing Date:</b> 22 February 1995 (22.02.95)  <b>(30) Priority Data:</b> 221,620                      1 April 1994 (01.04.94)                      US  <b>(71) Applicant:</b> MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037-0001 (US).  <b>(72) Inventors:</b> WAGNER, John, Ralph, Jr.; 300 Ashley Drive, Rochester, NY 14620 (US). MOUNT, Eldridge, Milford, III; 88 County Downs Circle, Fairport, NY 14450 (US).  <b>(74) Agents:</b> ROBERTS, Peter, William et al.; Mobil Oil Corpora- tion, 3225 Gallows Road, Fairfax, VA 22037-0001 (US).		<b>(81) Designated States:</b> AU, CA, CN, CZ, HU, JP, KR, NZ, PL, SK, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> BARRIER FILMS HAVING CARBON-COATED SURFACES  <b>(57) Abstract</b>  A carbon coated polymeric film is produced by Plasma Enhanced Chemical Vapor Deposition. An amorphous nylon layer having at least one exposed high energy surface is adhered to a polymeric substrate. Carbon is thereafter deposited on the exposed high energy surface by vapor deposition of a decomposable precursor in the presence of plasma.		

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BARRIER FILMS HAVING CARBON-COATED SURFACES

The present invention relates to barrier films and, in particular, to barrier films having at least one exposed high energy surface for receipt of a carbon coating.

5 Carbon coatings are known to provide certain barrier characteristics. For example, a carbon coating can inhibit the transmission of elements such as water and oxygen. Accordingly, carbon coatings are commonly applied to substrates (e.g., polymeric films), which otherwise would not possess these  
10 barrier characteristics. Films having such carbon coatings are often referred to as barrier films.

Carbon coatings can be deposited on substrates through various techniques. One preferred technique is Plasma Enhanced Chemical Vapor Deposition (PECVD), which allows carbon to be  
15 deposited on low-temperature substrates such as polymeric films. Particularly, this technique allows the deposition of carbon at lower reaction chamber temperatures, as compared to the reaction chamber temperatures required in other deposition processes. As a result, the lower reaction chamber temperature allows  
20 carbon to be deposited on low-temperature substrates.

The PECVD process is, however, a relatively slow and lengthy process, which in many cases renders such technique commercially impracticable. Accordingly, there exists a need in the art for a method which increases the rate of production  
25 of a PECVD barrier film, while at the same time maintaining the desirable barrier properties of a carbon-coated substrate.

The present invention, which addresses the needs of the prior art, provides a method for producing a polymeric film having barrier characteristics. The method includes the step  
30 of depositing a carbon coating on an exposed high energy surface of an amorphous nylon layer by vapor deposition of a decomposable precursor in the presence of plasma.

Preferably, the amorphous nylon layer is adhered to a polymeric substrate. Carbon is thereafter deposited on the  
35 exposed high energy surface by PECVD, preferably under dual frequency conditions.

The method preferably includes the step of applying a

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primary frequency of about 13.5 MHz to a first electrode positioned in a reaction chamber to generate the plasma and a secondary frequency of 90kHz to 450 kHz to a second electrode positioned in the chamber to facilitate deposition of the carbon coating on the exposed high energy surface.

The present invention also provides a method for increasing the production rate of a barrier film. The method includes the step of adhering an amorphous nylon layer having at least one exposed high energy surface to a polymeric substrate. The method includes the additional step of depositing a carbon coating on the exposed high energy surface by vapor deposition of a decomposable precursor in the presence of plasma.

The present invention also provides a polymeric film having barrier characteristics. The film is produced by the process of depositing a carbon coating on an exposed high energy surface of an amorphous nylon layer by vapor deposition of a decomposable precursor in the presence of plasma. The amorphous nylon layer is preferably adhered to a polymeric substrate.

As a result of the present invention, the time required to produce a carbon coated polymeric film is greatly reduced, thereby increasing the commercial practicality of PECVD techniques. Moreover, the resultant films provide an improved barrier to the transmission of oxygen and water.

In accordance with the present invention, a method is provided for producing a polymeric film having barrier characteristics. The method includes the step of depositing a carbon coating on an exposed high energy surface of a polymeric layer by vapor deposition of a decomposable precursor in the presence of plasma.

In one preferred embodiment, a layer of amorphous nylon is adhered to a polymeric substrate. The exposed surface of the nylon layer provides the aforementioned high energy surface. It is this high energy surface that receives the deposited carbon.

The amorphous nylon layer may be adhered to the substrate by a variety of techniques known in the art. For example, the

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nylon layer may be laminated onto a polymeric substrate by use of an adhesive. One particularly preferred method of securing a nylon layer to a polymeric substrate is accomplished by co-extruding a polymeric material with amorphous nylon, thereby  
5 providing a polymeric substrate having a layer of amorphous nylon on at least one side. Typically, a tie layer is employed to adhere the amorphous nylon to the polymeric substrate. For example, a material such as malic anhydride modified polypropylene can be employed as the tie layer. One such  
10 commercially available product is Atmer QF-500A.

The amorphous nylon employed in the present invention is preferably an amorphous co-polyamide based on hexamethylenediamine and a mixture of isophthalic and terephthalic acids. One such commercially available product is  
15 Dupont PA-3426.

The amorphous nylon layer provides a high energy surface, which is believed to facilitate the adhesion of deposited carbon thereto. Particularly, the exposed surface of the amorphous nylon exhibits a high "wettability" compared to other polymers.  
20 Wettability is believed to affect the ability of materials to intimately contact one another. In this regard, it has been demonstrated herein that the application of a polymeric layer having a high energy surface (such as amorphous nylon) to a polymeric substrate greatly reduces the time required to deposit  
25 a carbon coating via PECVD. It is therefore contemplated that other polymers exhibiting a similar wettability would also be effective in providing a high energy surface for receipt of a carbon coating.

Examples of polymeric substrates contemplated in the  
30 present invention include polypropylene, polyethylene, biaxial nylon and polyester. However, it is believed that other substrates, as long as such substrates are compatible with the material exhibiting the high energy surface, could be employed in the present invention.

35 The present invention also provides a method for increasing the production rate of a barrier film. The method includes the steps of adhering a polymeric layer having at least one exposed

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high energy surface to a polymeric substrate and, thereafter depositing a carbon coating on the exposed high energy surface by vapor deposition of a decomposable precursor in the presence of plasma. Again, this polymeric layer is preferably amorphous nylon.

As described earlier, the carbon coating is formed by the deposition of a decomposable precursor. A hydrocarbon gas having from 1 to 20 carbon atoms is used as the decomposable precursor. Acetylene is one such preferred precursor gas.

Upon the introduction of the decomposable precursor to the plasma, the precursor gas decomposes and is thereafter deposited on the exposed high energy surface as an amorphous carbon layer. This carbon coatings may range in thickness from 10 to 5000 Angstroms. The thickness of the amorphous carbon coatings will be primarily dependent on the amount of time allowed for deposition.

The plasma in the present invention is generated by the application of a primary radio frequency to a first electrode. This radio frequency excites the gas mixture flowing through the chamber, thereby forming a plasma. This gas mixture is preferably a mixture of the precursor gas mentioned above, e.g., acetylene, and an inert gas such as argon.

Apparatuses adapted for PECVD are commercially available. Such apparatuses generally include a chamber sized for receipt of a substrate. The apparatus additionally includes a vacuum pump for evacuating the chamber, means for introducing a gas mixture to the chamber under controlled conditions, and means for generating a plasma within the chamber.

In one particularly preferred embodiment, the plasma generation means includes distally spaced first and second electrodes, which together can be employed to introduce independent dual energy sources into the reaction chamber. A primary radio frequency of about 13.56 MHz is applied to the first electrode and a secondary radio frequency from 90 KHz to 450 KHz is applied to the second electrode. Preferably, the chamber serves as the ground (earth) for both radio frequencies.

The primary frequency generates the plasma (by exciting the

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gas mixture), while the secondary frequency is believed to facilitate the deposition of the carbon on the high energy surface by exciting the carbon molecules being deposited. This rationale is supported by the fact that a visible change in the plasma is observed upon application of this second radio frequency.

Other means of generating the plasma are also contemplated. For example, a primary radio frequency of about 2.45 GHz could be applied across the electrodes. In addition, lasers or magnetic fields could be employed to excite the gas mixture.

The chamber also includes a substrate holder plate for supporting the polymeric substrate to be coated. This substrate holder plate is preferably integral with the second electrode. In addition, the substrate holder plate may include either a flat or an arcuate support surface. It is contemplated that the use of an arcuate support surface would facilitate commercial production of the present invention.

The following Examples illustrate the invention.

#### EXAMPLE 1

Two control films were produced. A 1 mil thick oriented polypropylene film approximately 11" long by 15.5" wide was placed on a 10" long by 15.5" wide substrate holder plate attached to the second electrode. The substrate holder plate included an arcuate surface having a 40" radius of curvature. The film overhung the substrate holder plate along the length of such film to allow the film to be secured to the holder.

The chamber was pumped down to about 1 mTorr. An acetylene/argon gas mixture was then introduced into the chamber at a flow rate of 100 sccm, 70% of the mixture being acetylene. The pressure within the chamber was increased to a reaction pressure of about 100 mTorr by use of a gate valve located at the inlet of the vacuum pump. A primary frequency of 13.5 MHz at a power level of 100 watts was applied to the first electrode and a secondary frequency of 95 kHz at a power level of 25 watts was applied to the second electrode.

The substrate was coated for approximately 300 seconds. Thereafter, the gas mixture was shut off and the chamber was



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pumped down again to about 1 mTorr. The chamber vacuum was then broken by bleeding in dry nitrogen gas and the respective coated substrate was removed.

The two control films were thereafter tested. The first control film exhibited an oxygen transmission rate ( $TO_2$ ) of 0.4 cc  $O_2$ /100in<sup>2</sup>/atm/24hr at 23°C and 0% relative humidity and a water vapor transmission rate (WVTR) of 0.02 g  $H_2O$ /100in<sup>2</sup>/atm/24hr at 100°F and 90% relative humidity. The second control film exhibited an oxygen transmission rate of 0.6 cc  $O_2$ /100in<sup>2</sup>/atm/24hr at 23°C and 0% relative humidity and a water vapor transmission rate of 0.09 g  $H_2O$ /100in<sup>2</sup>/atm/24hr at 100°F and 90% relative humidity.

Accordingly, the average control oxygen transmission rate was 0.5 cc  $O_2$ /100in<sup>2</sup>/atm/24hr at 23°C and 0% relative humidity and the average control water vapor transmission rate was 0.055 g  $H_2O$ /100in<sup>2</sup>/atm/24hr at 100°F and 90% relative humidity.

#### EXAMPLE 2

Barrier films in accordance with the present invention were produced by co-extruding amorphous nylon with polypropylene into a base sheet that was subsequently biaxially oriented. Resin pellets of Dupont nylon PA-3426 were employed, along with a tie layer of Atmer QF-500A. The oriented film was approximately 1 mil thick, the amorphous nylon layer representing approximately 6% or .06 mils of the total film thickness.

A polymeric sample approximately 11" long by 15.5" wide was placed on the substrate holder plate attached to the second electrode and described above in Example 1.

The chamber was pumped down to about 1 mTorr. An acetylene/argon gas mixture was then introduced into the chamber at a flow rate of 60 sccm, approximately 83% of the mixture being acetylene. The pressure within the chamber was increased to a reaction pressure of about 100 mTorr by use of a gate valve located at the inlet of the vacuum pump. A primary frequency of 13.5 MHz at a power level of 100 watts was applied to the first electrode and a secondary frequency of 95 kHz at a power level of 25 watts was applied to the second electrode.

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The substrate was coated for approximately 60 seconds. Thereafter, the gas mixture was shut off and the chamber was pumped down again to about 1 mTorr. The chamber vacuum was then broken by bleeding in dry nitrogen gas and the respective coated  
5 substrate was removed.

The polymeric sample was thereafter tested. The sample film exhibited an oxygen transmission rate of 0.42 cc  $O_2$ /100in<sup>2</sup>/atm/24hr at 23°C and 0% relative humidity and a water vapor transmission rate of 0.024 g  $H_2O$ /100in<sup>2</sup>/atm/24hr at 100°F  
10 and 90% relative humidity.

Additional polymeric samples were prepared under varying test conditions. The measured results from all of the polymeric samples, i e., samples 1-8, are set forth in the following table:

SAMPLES	TO <sub>2</sub>	WVTR	PRESSURE (mTorr)	FLOW		PRIMARY POWER (watts)	SECONDARY POWER (watts)	TIME (sec.)
				C2H2	Ar			
Control 1	0.4	0.02	100	70	30	100	25	300
Control 2	0.6	0.09	100	70	30	100	25	300
Sample 1	0.42	0.024	100	50	10	100	25	60
Sample 2	0.18	0.005	100	50	10	50	25	60
Sample 3	0.11	0.015	100	50	10	75	25	60
Sample 4	0.10	0.024	100	50	10	75	25	45
Sample 5	0.18	0.020	100	50	10	75	25	30
Sample 6	0.26	0.062	100	50	10	75	25	15
Sample 7	0.07	0.036	150	50	10	75	25	30
Sample 8	0.09	0.051	100	50	10	50	25	30

TO<sub>2</sub>: cc/100 in<sup>2</sup>/atm/24hr at 23°C and 0% R.H.

WVTR: g/100in<sup>2</sup>/atm/24hr at 100°F and 90% R.H.

FLOW: Standard cubic centimeter (sccm)

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It is readily apparent from the test data set forth above that a barrier film can be produced by the deposition of carbon on an exposed high energy surface of an amorphous nylon layer. It is particularly significant that the rate of producing such  
5 a barrier film can be increased by approximately a factor of 10, i.e., the coating time is decreased from approximately 300 seconds to about 15 to 60 seconds. It is also significant that the resultant film exhibits a markedly decreased rate of oxygen transmission, while improving, or at the minimum maintaining,  
10 the level of water transmission.

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**CLAIMS**

1. A polymeric film having barrier characteristics, which film comprises an amorphous nylon layer on an exposed high energy surface of which layer is deposited a carbon coating, which coating is preparable by vapour deposition of a decomposable precursor in the presence of a plasma.

2. A polymeric film according to claim 1, wherein the nylon layer is adhered to, or coextruded with, a polymeric substrate.

3. A method of producing a polymeric film having barrier characteristics, which method comprises depositing a carbon coating on an exposed high energy surface of an amorphous nylon layer by vapor deposition of a decomposable precursor in the presence of a plasma.

4. A method according to Claim 3, wherein the deposition is accomplished under dual frequency conditions.

5. A method according to Claim 3 or 4, wherein the depositing step includes applying a primary radio frequency to a first electrode positioned in a reaction chamber to generate the plasma and applying a secondary frequency of 90kHz to 450 kHz to a second electrode positioned in the reaction chamber to facilitate deposition of the carbon coating on the exposed high energy surface.

6. A method according to Claim 3, 4 or 5, wherein the second electrode includes a substrate holder plate and, the amorphous nylon layer is positioned on the substrate holder for receipt of the carbon coating on the exposed high energy surface.

7. A method according to any preceding claim, wherein the decomposable precursor comprises a hydrocarbon having from 1 to 20 carbon atoms.

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8. A method according to claim 7, wher in the hydrocarbon comprises acetylene.

9. Use, in order to increase the production rate in the  
5 preparation of a polymeric film having barrier characteristics  
and comprising a deposited carbon coating preparable by vapour  
deposition of a decomposable precursor in the presence of a  
plasma, of an amorphous nylon layer on an exposed high energy  
surface of which layer the carbon coating is deposited.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/02799

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B32B 9/00; B05D 3/06

US CL : 427/537, 569, 576; 428/336, 408

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/537, 569, 576; 428/336, 408

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,756,964 (KINCAID ET AL.) 12 July 1988, see entire document.	1-5, 9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/02799

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-8.  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

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2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.